SEMI QUANTITATIVE DETERMINATION OF COAL MINERALS BY X-RAY DIFFRACTOMETRY

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INTRODUCTION

The purpose of this paper is to present and support the argument that abundance estimates of the minerals in coal based upon x-ray diffraction data can only be considered semi-quantitative with expected errors of determination of 10 percent or more of the reported values. The compositional and physical characteristics of the low temperature ash components of coal relative to the preparation and mounting of ash for XRD analysis must also be considered.

MINERALS IN COAL

The minerals commonly found in coal are listed in Table 1. In the average coal, clay minerals may constitute up to 60 weight percent of the mineral matter (1,2). Quartz is usually the second most abundant mineral, with up 20 weight percent being common. The carbonate minerals (calcite, siderite and to a lesser extent, dolomite and ankerite) and the iron disulphide minerals (pyrite and marcasite) make up, on the average, about 10 weight percent each group. Sulphate minerals of calcium and iron and the feldspar minerals are commonly present but rarely in concentrations of more than a few weight percent. Except for unusual cases such as the sulphide rich coals of the northern Illinois Basin, the occurrence of the other minerals in concentrations exceeding a few percent is rare. It must, however, be kept in mind that the mineralogy of the inorganic portion of coal shows systematic variation both geographically and locally reflecting the geochemistry of the original peat forming environment (3). As a result, "average" values of concentration may have little practical meaning.

Most coals considered for conversion processes such as liquifaction, and thereby those of prime interest to chemists, are generally high in ash (>10 weight percent) and sulfur (>1 weight percent). In such coals, illite would invariably be the dominant clay material, constituting, in some coals, up to half or more of the mineral content. Most of the sulfur contained in these coals will be in the form of pyrite although marcasite may be locally dominant (4).

QUANTIFICATION BY X-RAY DIFFRACTION

The most commonly employed quantitative XRD procedure used to evaluate the concentration of mineral components in a multicomponent mixture of minerals compares the Bragg intensity data of unknowns to those generated from a suite of known standard samples. Mineral specimens are acquired to represent each of the minerals expected in the unknowns. The specimens are ground to a uniformly small size (less than 44 microns) and mixed together in concentrations which represent the range of concentrations expected for each mineral. An internal standard such as calcium fluoride, aluminum oxide or powdered aluminum is usually added in order to monitor and correct for variations in sample absorption and instrumental variables. Working curves are then prepared by plotting the ratio of intensity (preferably integrated intensity) of the Bragg reflection chosen to quantify the mineral to that chosen for the standard versus the weight percent of the mineral in the standard samples.

This procedure will provide analyses of high precison provided certain basic assumptions are met: (1) the high composition and crystallinity (degree of ordering) of the individual minerals in the unknowns are both reasonably constant from sample to sample and (2) the composition and crystallinity of the standard minerals chosen for the preparation of the standard samples reasonably duplicate the composition and crystallinity of the respective minerals in the unknowns. The purpose of the following discussion is to demonstrate that, in the case of coal minerals, neither of the above assumptions is valid and as a result, any such quantitative procedure will reflect the inherent degree of departure from these basic assumptions and will therefore be semi-quantitative. Other procedures using data normalized to the total integrated intensity and quantification procedures utilizing weighting factors based upon standard chemical formulae for the minerals can be used but with no improvement in quantitative errors (5,6).

Illite and pyrite were specifically cited in the above discussion to make a point relative to the precision and accuracy with which coal minerals can be quantified by XRD. First, illite is NOT a mineral. Illite is "...a general term for the clay mineral constituents of argillaceous sediments belonging to the mica group (7). To a clay mineralogist, the term illite is synonomous with variability in both composition and crystallinity (8). The situation is even further complicated by the fact that much of the material in coal referred to a "illite" is actually an illite dominated mixed layered clay wherein the illite lattices are randomly interstratified with 14A clay lattices; usually chlorite. This mixing of clay mineral lattices further adds to the inherent variability in both composition and crystallinity of the illite material. The constitution of "illite" can therefore be expected to vary significantly from sample to sample. It should be quite apparent from the above discussion that no "standard" illite exists that could be used to represent illite in standard samples.

The iron disulphides may represent 10 weight percent or more of high ash-sulphur coal ashes. Usually, pyrite is the major disulphide. Pyrite occurs in coal in a number of morphological forms and sizes (9). Not only does the pyrite in coal vary in morphology and size but also in stoichiometry and crystallinity. Studies have been conducted in the author's laboratory on cut and polished surfaces of coal blocks wherein the blocks have been exposed to the atmosphere and the pyrites observed over a period of time. Some pyrite grains, the

euhedral forms, remain bright and show little tendency to react. The massive forms of pyrite, on the other hand, show a wide variation in apparent reactivity with crystals of ion sulfates being observed to form on some pyrite surfaces within a matter of hours and in some cases, within minutes.

Another study involved in quantification of pyrite in different coal lithotypes. Coals are described megascopically based upon the degree of bright and dull banding. Zones are delineated within the coal and designated as a "lithotype" based on the relative percentage of bright and dull bands within the zone (10). Dominantly bright bands are called "VITRAIN", dull bands, DURAIN and those intermediate between the two; "CLARAIN". Although the designation as to lithotype is solely made depending upon megascopic description, the lithotypes differ in basic organic composition as illustrated by the data for the Waynesburg Coal shown in Table 2.

TABLE 2. COMPOSITION OF LITHOTYPES OF THE WAYNESBURG COAL

LITHOTYPE	%VITRINITE	%EXINITE	%INERTINITE	%MINERAL MATTER
Vitrain	93.1	1.8	2.4	2.7
Clarain	84.2	4.4	5.6	5.8
Durain	43.4	17.8	24.9	13.9

The low temperature ash of each lithotype was then submitted to XRD analysis. The integrated intensities of each of the selected analytical Bragg reflections selected for the individual minerals were summed for all minerals present in each sample to give a "total integrated intensity". This value was then divided into the integrated intensity of the pyrite analytical Bragg reflection to give the "percent of total integrated intensity". The data are summarized in Figure 1. It is apparent that there is a systematic relationship between the composition/crystallinity of the pyrite and the basic organic makeup of the coal. Most important is the observation that equal concentrations of pyrite give different intensity responses. Volume for volume, the pyrite contained within the bright coal (Vitrain) showing significantly higher Bragg intensities than the pyrite contained in the duller coals.

To compound the problem, marcasite for reasons unknown to the author, does not show the intensity reponse, volume for volume as pyrite. It has been the author's experience that the marcasite coals that have been shown by optical examination to be insignificant concentration show almost no indication of being present on a diffractogram generated from the low temperature ash.

It must be apparent from the above discussion that the great number of variables other than concentration affect the intensities of mineral pattern as observed on a diffractogram. Inasmuch as they cannot be monitored and compensated for mathmetically, these variations must be reflected in the error of determination. This would be true regardless of the quantification procedure employed. The conclusion, therefore, is that the inherent variability in composition and/or crystallinity that exists within the major mineral components of the low temperature ashes of coal will be reflected in the statistical error of determination and that error will be of sufficient magnitude to preclude the use of the term "quantitative" to describe the procedure. Therefore, any procedure using x-ray diffraction to determine the minerals in coal must be considered semi-quantitative at best.

SAMPLE PREPARATION & MOUNTING

Any procedure for the preparation and mounting of coal low temperature ashes for XRD analysis MUST take two properties of the material into account: (1) minerals exist which react with water to produce acidic solutions (the iron disulphides) which in turn dissolve acid soluble components such as calcite and (2) the clay minerals by virtue of exceptionally well developed (001) cleavage surfaces have a dominant platey crystal form. The significance of the first attribute is that the ashes cannot be placed in water thereby precluding certain sample preparation techniques such as dispersion in water followed by vacuum mounting on filters or ceramic blocks. The second characteristic, possession of a platey crystal form, precludes the attainment of the theoretically required randomly oriented sample. Those who work with the clay minerals, realizing a random sample cannot be prepared and that the clay particles will deposit in preferred orientation, purposely prepare and mount the samples such that the preferred orientation of the individual platelets is maximized and thereby minimize any variations in diffraction intensity due to variations in particle alignment within the sample. The orientation of the clay platelets parallel to the sample surface positions the "C" crystallographic axis perpendicular to the sample surface. Because the diagnostic interplanar spacing for the clay minerals is along the "C" crystallographic direction, such an orientation is ideal for clay mineral identification. The simplest method to mount a low temperature ash for XRD analysis is to press the ash onto the surface of a pellet prepared from the coal from which the ash was derived.

FUTURE PROSPECTS

A few years ago, and ad hoc group of workers interested in coal minerals, The Mineral Matter in Coal Group, prepared and distributed a round-robin low temperature ash to ten laboratories. Each laboratory was to prepare, mount and quantify the mineral components in the ash by their respective XRD techniques. The data were then compared. Even though a wide variety of techniques was used for each phase of the analysis, with the exception of the clay mineral estimates made by one laboratory (significantly lower than the others) and the pyrite estimate made by another (too high), the data compared reasonably well. The averages of all the submitted estimates are summarized in Table 3.

TABLE 3. RESULTS OF ROUND ROBIN L.T.A. ANALYSIS

MINERAL	AVE. CONC. WT%	S.DEV.	C.V.
Illite+Mix L	30	7.07	0.24
Kaolinite	18	4.85	0.27
Quartz	21	6.31	0.30
Calcite	10	3.59	0.36
Pyrite	18	4.93	0.27

Another objective of the exercise was to discuss the results and procedures used and come to some agreement on a "standard" procedure for sample preparation, mounting and quantification that would be acceptable to all the workers. The agreement that was reached was that no agreement would be forthcoming on any of the phases of the analysis. With no one procedure demonstratably better than the other, each laboratory was expected to maintain their own procedure. As long as a procedure is scientifically and analytically sound and reflects a thorough understanding of the characteristics of minerals contained in coal and the requirements and limitations of x-ray diffraction, one procedure will probably be as good as another but none will be better than semi-quantitative. With all its shortcomings, x-ray diffraction is still the best and most practical method for the estimation of the abundance of the individual minerals in coal.

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TABLE 1

COMMON COAL MINERALS

Major	Silicates	Clay Minerals	Kaolinite	$Al_2Si_2O_5(OH)_4$
			Illite	a
			Mixed Layer	b
			Chlorite	$(MgfFeAl)_6(SiAl)_4O_{10}(OH)_8$
			Quartz	SiO_2
Minor		Carbonates	Calcite	$CaCO_3$
			Dolomite	$(Ca,Mg)(CO_3)_2$
			Ankerite	$Ca(Fe,Mg)CO_3$
			Siderite	$FeCO_3$
		Disulfides	Pyrite	FeS_2 (cubic)
			Marcasite	FeS_2 (orthorhombic)
		Sulfates	Coquimbite	$Fe_2(SO_4)_3\ 9H_2O$
			Szmolnokite	$FeSO_4\ H_2O$
			Gypsum	$CaSO_4\ 2H_2O$
			Bassanite	$CaSO_4\ 1/2H_2O$
			Anhydrite	$CaSO_4$
			Jarosite	$KFe_3(SO_4)_2(OH)_6$
		Feldspars	Plagioclase	$(NaCa)Al(AlSi)Si_2O_8$
			Orthoclase	$KAlSi_3O_8$

[a]Illite has a composition similar to muscovite-$KAl_2(Si_3Al)O_{10}(OH)_2$, except for less K^+ and more SiO_2 and H_2O

[b]Mixed layered clays are usually randomly interstratified mixtures of illitic lattices with montmorillonitic and/or chloritic lattices.

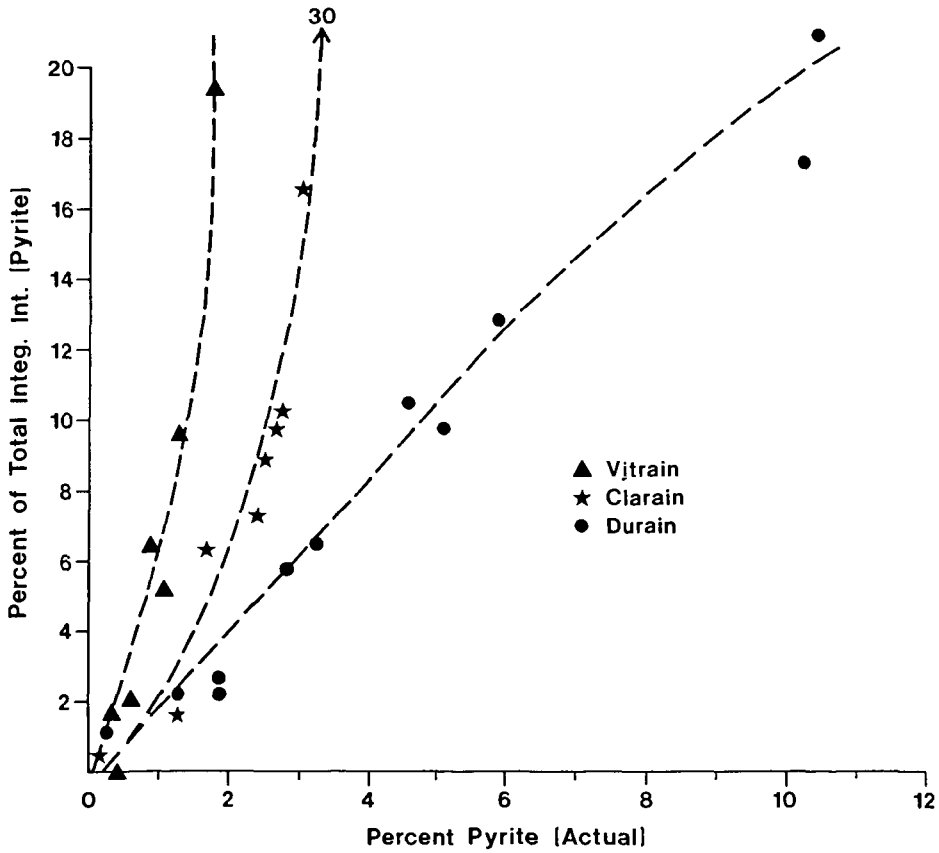

Figure 1. Relationship between actual pyrite composition and relative percent total integrated intensity of pyrite in low temperature ashes of Waynesburg coal lithotypes.